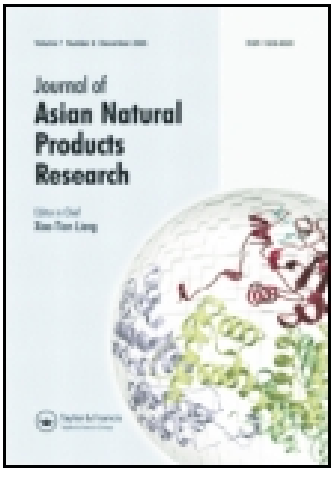

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Resin glycosides from *Porana duclouxii*

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A new intact resin glycoside (**3**) and two glycosidic acids (**1** and **2**), all having a common trisaccharide moiety and (11*S*)-hydroxytetradecanoic acid or (3*S*,11*S*)-dihydroxytetradecanoic acid as the aglycone, were obtained from the roots of *Porana duclouxii*. Their structures were elucidated by spectroscopic analyses and chemical correlations. These compounds represent the first examples of resin glycosides from the genus *Porana.*

Keywords: *Porana duclouxii*; resin glycoside; triglycoside

1. Introduction

The genus *Porana* (Fam. Convolvulaceae) consists of about 20 species occurring in subtropical and tropical areas worldwide [1]. Some plants of this genus, such as *Porana racemosa* and *Porana mairei*, are recorded in Chinese folk medicine for the treatment of cough, nameless swelling, overworked pain, and severe fever [2]. Previous phytochemical studies on this genus led to the isolation of ecdysteroids, coumarins, sterols, and flavanoids [3–6]. Resin glycosides are known to be characteristic of constituents in Convolvulaceae, which have been obtained from more than 34 species belonging to six genera (*Ipomoea*, *Merremia*, *Convolvulus*, *Operculina*, *Cuscuta*, and *Calystegia*) of this family [7]. However, they have not been reported from any *Porana* species so far.

Porana duclouxii, a Chinese endemic species, is distributed in Hubei, Yunnan and Sichuan provinces of Chinese mainland [1]. In our phytochemical study on *P. duclouxii*, a crude resin glycoside fraction was obtained. This paper describes the isolation and characterization of an intact resin glycoside and two glycosidic acids from the fraction, which were trivially named poranaside A (**3**), poranic acid A (**1**), and poranic acid B (**2**), respectively.

2. Results and discussion

Poranic acid A (**1**) was obtained as a white powder, with m.p. 175–178°C. Its molecular formula, $C_{32}H_{58}O_{16}$, was determined from NMR (^{1}H and ^{13}C) and ESI-MS data and confirmed by HR-ESI-MS. The negative ion ESI-MS of **1** exhibited an $[M-H]^-$ ion peak at *m/z* 697 as well as a series of fragment ions at *m/z* 551 [697–146 $(C_6H_{10}O_4)]^-$, 389 [551–162 $(C_6H_{10}O_5)]^-$, and 243 [389–146 $(C_6H_{10}O_4)]^-$. The ^{1}H NMR signals of **1** displayed recognizable signals for three anomeric protons [δ_H 6.33 (br s); 5.87 (d, $J = 7.0$ Hz); 4.87 (d, $J = 7.5$ Hz)]. The ^{13}C NMR spectrum gave 32 signals, of which 18 carbons were assignable to a trisaccharide moiety and 14 carbons to the aglycone

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moiety. All the above evidence indicated that **1** was a triglycoside with a hydroxytetradecanoic acid as the aglycone. The ^{1}H and ^{13}C NMR signals of **1** were carefully assigned with the aid of H–H COSY, HSQC, and HMBC experiments (Table 1). Comparing the ^{1}H and ^{13}C NMR chemical shifts of **1** and the related triglycosides in the literatures [8,9], this compound was very similar to cuscutic acid A2 [8], except the inner D-fucose in cuscutic acid A2 was substituted by a D-quinovose in **1**. By complete acidic hydrolysis, **1** furnished 11-hydroxytetradecanoic acid, D-quinovose, D-glucose, and L-rhamnose. The absolute configuration of 11-hydroxytetradecanoic acid was

Table 1. ^{1}H and ^{13}C NMR spectral data of compounds **1**, **2**, and **3**.

	1		**2**		**3**	
Position	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
Qui-1	4.87 (d, 7.5)	102.1	4.87 (d, 7.5)	102.1	4.81 (d, 7.4)	102.3
2	4.34 (dd, 7.5, 8.8)	79.6	4.34 (dd, 7.5, 8.5)	79.5	4.40$^{\alpha}$	78.8
3	4.42 (dd, 9.0, 8.8)	79.0	4.41 (dd, 9.0, 8.5)	79.0	4.32 (dd, 9.0, 8.5)	79.3
4	3.59 (dd, 9.0, 9.0)	76.7	3.59 (dd, 9.0, 9.0)	76.7	3.59 (dd, 9.0, 9.0)	76.6
5	3.70 (m)	72.2	3.70 (m)	72.2	3.72 (m)	72.3
6	1.55 (d, 6.0)	18.4	1.55 (d, 6.1)	18.4	1.61 (d, 6.0)	18.4
Glc-1	5.87 (d, 7.0)	101.7	5.87 (d, 7.2)	101.7	5.97 (d, 7.2)	101.2
2	4.27 (dd, 7.2, 8.9)	78.6	4.27 (dd, 7.2, 8.9)	78.6	4.24$^{\alpha}$	77.8
3	4.25$^{\alpha}$	78.9	4.25$^{\alpha}$	78.9	4.23$^{\alpha}$	79.2
4	4.10 (t, 8.9)	72.2	4.10 (t, 8.9)	72.2	4.07 (t, 9.0)	72.2
5	3.86 (m)	77.5	3.86 (m)	77.5	3.85$^{\alpha}$	77.7
6	4.46 (dd, 11.4, 2.6)	62.9	4.43 (dd, 9.2, 2.3)	62.9	4.43 (dd, 9.2, 2.3	62.8
	4.26 (11.4, 6.7)		4.26$^{\alpha}$		4.27$^{\alpha}$	
Rha-1	6.33 (br s)	101.8	6.34 (br s)	101.9	6.41 (br s)	101.4
2	4.76 (br s)	72.1	4.74 (br s)	72.1	4.70 (br s)	72.2
3	4.69 (dd, 9.2, 3.2)	72.4	4.66 (dd, 9.2, 3.3)	72.4	4.71 (dd, 9.2, 3.3)	70.0
4	4.32 (dd, 8.9, 3.3)	74.1	4.32 (dd, 8.9, 3.3)	74.1	5.94 (t, 9.4)	75.6
5	5.00 (m)	69.4	5.00 (m)	69.4	5.10 (m)	66.9
6	1.80 (d, 6.1)	18.6	1.80 (d, 6.2)	18.6	1.63 (d, 6.3)	18.3
Ag-1		177.1		175.3		172.7
2	2.48 (t, 7.4)	35.2	2.87 (br d, 6.0)	43.8	2.70 (dd, 6.4, 3.1)	43.2
3	1.73 (m)	25.6	4.53 (m)	68.4	4.53 (m)	68.0
4	1.34$^{\alpha}$	29.6	1.70 (m)	37.9	1.64–1.70 (m)	37.9
5–9	1.69 (m)	25.1	1.68 (m)	25.2	1.69 (m)	25.2
	1.20–1.40$^{\alpha}$	29.5	1.54 (m)	26.1	1.63 (m)	26.0
	1.20–1.40$^{\alpha}$	29.8	1.26–1.47$^{\alpha}$	30.0	1.26–1.44$^{\alpha}$	29.9
	1.20–1.40$^{\alpha}$	29.9	1.26–1.47$^{\alpha}$	30.0	1.26–1.44$^{\alpha}$	30.0
	1.20–1.40$^{\alpha}$	30.1	1.26–1.47$^{\alpha}$	30.3	1.26–1.44$^{\alpha}$	30.3
10	1.65–1.80 (m)	34.6	1.63–1.77 (m)	34.6	1.65–1.74 (m)	34.6
11	3.88 (m)	80.2	3.88 (m)	80.1	3.88 (m)	80.6
12	1.77 (m)	37.3	1.75 (m)	37.3	1.78 (m)	37.3
	1.60 (m)		1.58 (m)		1.60 (m)	
13	1.57 (m)	18.6	1.65 (m)	18.8	1.53 (m)	18.5
14	0.90 (t, 7.1)	14.2	0.90 (t, 7.1)	14.2	0.91 (t, 6.1)	14.2
*O*Me					3.61 (s)	51.1
ang-1						167.7
2						128.4
3					5.88 (m)	137.3
4					2.07 (dd, 7.2, 1.4)	16.0
2-Me					2.00 (d, 1.4)	20.9

$^{\alpha}$ Signals are overlapping, **S** in ppm, *J* in Hz.

determined as 11*S* by comparison of specific rotation of methyl ester with those obtained from Mexican jalap roots [10]. The absolute configurations of sugars were determined by direct comparison of specific optical rotation with authentic samples and confirmed by GC–MS with their TMSi-derivatives, respectively. The connectivities between the hydroxyl fatty acid aglycone and oligosaccharide, and among monosaccharides in **1** were supported by its HMBC spectrum. The long-range correlations were observed as follows: H-1 (δ_H 4.87) of Qui with C-11 (δ_C 80.2) of the aglycone (11*S*-convolvulinolic acid), H-1 (δ_H 5.87) of Glc with C-2 (δ_C 79.6) of Qui, H-1 (δ_H 6.33) of Rha with C-2 (δ_C 78.6) of Glc. These data confirmed that the linkage of **1** was Rha-(1 → 2)-Glc-(1 → 2)-Qui-(1 → 11)-aglycone. Furthermore, the component sugar moieties were determined to be β-quinopyranosyl, β-glucopyranosyl, and α-rhamnopyranosyl, respectively, by vicinal ^1H–^1H coupling constants (Table 1). Accordingly, **1** was characterized as (11*S*)-hydroxytetradecanoic acid 11-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-quinovopyranoside (Figure 1).

The molecular formula of poranic acid B (**2**), with m.p. 180–183°C, was determined as $C_{32}H_{58}O_{17}$, by the negative ESI-MS, showing the pseudo-molecular ion peak at *m/z* 713 $[M-H]^-$, along with fragment peaks at *m/z* 567 and 405, all of which were 16 mass units (OH) more than those corresponding ions of **1**. The ^1H and ^{13}C NMR spectra of **2** were superimposable on those of **1** except for signals due to the aglycone moiety. Moreover, the HMBC and ^{13}C NMR spectra demonstrated that the oligosaccharide moieties of **1** and **2** were identical. On mild acid hydrolysis, compound **2** afforded D-quinovose, D-glucose, L-rhamnose, and (3*S*, 11*S*)-dihydroxytetradecanoic acid (ipurolic acid) [11,12]. Thus, **2** was characterized as (3*S*,11*S*)-dihydroxytetradecanoic acid 11-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-quinovopyranoside (Figure 1).

Poranaside A (**3**) had a molecular formula of $C_{38}H_{66}O_{18}$, as determined from a quasi-molecular ion at *m/z* 811.4316 $[M+H]^+$ in the positive ion HR-ESI-MS. Its ^1H and ^{13}C NMR spectra (Table 1) displayed characteristic signals for a glycosidic acid core closely similar to poranic acid B (**2**), as well as additional resonances indicating the presence of a methoxyl group [δ_H 3.61 (3H, s)/δ_C 51.1] and a short organic acid moiety (angeloyl moiety). The signals readily distinguished for an olefinic methine at δ_H 5.88 (m), an olefinic tertiary methyl group at δ_H 2.00 (d, $J = 1.4$ Hz), and an olefinic secondary methyl group at δ_H 2.07 (dd, $J = 7.2$, 1.4 Hz) in the ^1H NMR spectrum, and five correspounding carbon resonances at δ_C 167.7, 137.3, 128.4, 20.9, and 16.0 in the ^{13}C NMR spectrum (Table 1) which were due to the angeloyl moiety [13]. Compound **3** was then subjected to saponification with 5% KOH and the products fractionated into organic and glycosidic acid

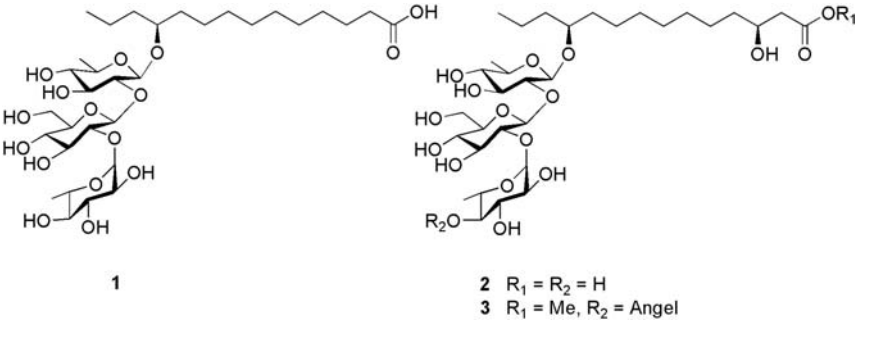

Figure 1. Structures of **1**, **2**, and **3**.

fractions. The former examined by GC–MS gave a peak corresponding to angelic acid, with EI-MS ions at *m/z* 100 $[M]^+$(100), 85 (29), 72 (0.8), 55 (86), 53 (16), and 39 (25). The glycosidic acid fraction furnished poranic acid B (**2**), which was confirmed by ^{1}H and ^{13}C NMR and HPLC. The long-range correlations were observed from OCH_3 (δ_H 3.61) to the aglycone carbon (δ_C 172.7), and from H-4 (δ_H 5.94) of Rha to the angeloyl carbon (δ_C 167.7) in the HMBC spectrum. The HMBC information indicated that the aglycone was a methyl ester, while the angeloyl moiety was located at C-4 of Rha. Comparing the NMR spectral data of **3** with its glycosidic acid core (**2**), the signal at 4-H of Rha was shifted toward downfield by 1.62 ppm, and the C-1 of aglycone was shifted toward upfield by 2.6 ppm (Table 1), which further confirmed the linkage of **3**. Therefore, the structure of poranaside A (**3**) was characterized as (3*S*,11*S*)-dihydroxytetradecanoic acid 11-*O*-(4-*O*-angeloyl)-α-L-rhamnopyranosyl-(1 → 2)-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-quinovopyranoside, methyl ester (Figure 1).

3. Experimental

3.1 General experimental procedures

Optical rotations were obtained on WZZ-2B automatic polarimeter (Precision Instrument Co., Shanghai, China); melting point was measured using a X-4 micromelting point apparatus (Cany Precision Instruments Co., Shanghai, China). The ^{1}H, ^{13}C, and 2D NMR spectra were recorded on a Bruker DRX-400 instrument (Bruker BioSpin GmbH Company, Rheinstetten, Germany) using TMS as an internal standard. EI-MS and HR-ESI-MS data were obtained on an API QSTAR mass spectrometer (Applied Biosystem/MSD Sciex, Concord, ON, Canada). Preparative HPLC was performed with a Waters 1525 Binary HPLC pump and a Waters 2414 refractive index detector using a YMC-Pack ODS-A column (5 μm, 250 mm × 20 mm). For column chromatography (CC), silica gel 60 (200–300 mesh, Qingdao Marine Chemical Ltd, Qingdao, China), Develosil ODS (50 μm, Nomura Chemical Co. Ltd., Osaka, Japan), and Sephadex LH-20 (GE Healthcare, Uppsala, Sweden) were used. Analytical GC was carried out on a Shimadzu GCMS-QP2000 Plus apparatus (Shimadzu Corporation, Tokyo, Japan) with an ionization energy of 70 eV.

3.2 Plant material

The roots of *P. duclouxii* were collected in Shennongjia, Hubei, China, in February 2012, and identified by Prof. Zhang Daigui (Key Laboratory of Plant Resources Conservation and Utilization, Jishou University). A voucher specimen (zdg3431) has been deposited at Jishou University.

3.3 Extraction and isolation

The powdered air-dried roots of *P. duclouxii* (150 g) were extracted with methanol thrice in an ultrasonic bath, each for 48 h at room temperature, and the extract was concentrated under reduced pressure to give 80 g of residue. The residue was suspended in water and then extracted with EtOAc. A lot of emulsion layer occurred between water and EtOAc. The emulsion layer was concentrated under reduced pressure and subjected to Sephadex LH-20 column chromatography to give a crude resin glycoside fraction (R, 5.0 g). A part of R (2.0 g) was further subjected to ODS column chromatography, using MeOH/H_2O mixtures of decreasing polarities (80:20 to 95:5) to give four subfractions (R_1–R_4). R_1 (150 mg) was separated by preparative HPLC using MeOH/H_2O (8:2, v/v) with a flow rate of 5 ml/min. Each peak was collected by manual recycling, to afford poranaside A (**3**) (30 mg, t_R 45 min). However, other efforts to isolate individual components from these sub-fractions were unsuccessful.

The resin glycoside fraction (2.0 g) was treated with 5% KOH at 85°C for 4 h. The reaction mixture was acidified to pH 4.0

and extracted with Et_2O (50 ml × 3). The aqueous layer was further extracted with *n*-BuOH (3 × 100 ml), and then the *n*-BuOH layer was concentrated *in vacuo* to yield a residue (540 mg), which was subjected to Sephadex LH-20 CC using MeOH to afford a glycosidic acid fraction (300 mg). A portion (100 mg) of this fraction was subjected to preparative HPLC using MeOH/H_2O (7:3) with a flow rate of 5 ml/min to obtain poranic acids A (**1**) (28 mg, t_R 35 min), B (**2**) (36 mg, t_R 60 min).

3.3.1 *Poranic acid A (**1**)*

White powder, m.p. 175–178°C, $[\alpha]_D^{20}$ −24.0 (*c* 0.3, MeOH); For ^{1}H NMR (400 MHz, C_5D_5N) and ^{13}C NMR (100 MHz, C_5D_5N) spectroscopic data, see Table 1; positive ion ESI-MS *m/z*: 721 $[M + Na]^+$; negative ESI-MS *m/z*: 697 $[M-H]^-$, 551, 389, 243; HR-ESI-MS *m/z*: 697.3646 $[M-H]^-$ (calcd for $C_{32}H_{57}O_{16}$, 697.3652).

3.3.2 *Poranic acid B (**2**)*

White powder, m.p. 180–183°C, $[\alpha]_D^{20}$ −20.0 (*c* 0.3, MeOH); For ^{1}H NMR (400 MHz, C_5D_5N) and ^{13}C NMR (100 MHz, C_5D_5N) spectroscopic data, see Table 1; positive ion ESI-MS *m/z*: 737 $[M + Na]^+$; negative ESI-MS *m/z*: 713 $[M-H]^-$, 567, 405; HR-ESI-MS *m/z*: 713.3592 $[M-H]^-$ (calcd for $C_{32}H_{57}O_{17}$, 713.3601).

3.3.3 *Poranaside A (**3**)*

Colorless syrup, $[\alpha]_D^{20}$ −14.0 (*c* 0.1, MeOH); For ^{1}H NMR (400 MHz, C_5D_5N) and ^{13}C NMR (100 MHz, C_5D_5N) spectroscopic data, see Table 1; positive ion ESI-MS *m/z*: 811 $[M + H]^+$, 833 $[M + Na]^+$; negative ESI-MS *m/z*: 845 $[M + Cl]^-$, 809 $[M-H]^-$; HR-ESI-MS *m/z*: 811.4316 $[M + H]^+$ (calcd for $C_{38}H_{67}O_{18}$, 811.4322).

3.4 *Acid hydrolysis of 1 and 2*

Compounds **1** and **2** (13 and 15 mg, respectively) were separately dissolved in 5% H_2SO_4 (2 ml) and heated at 95°C for 1 h. The reaction mixture was diluted with H_2O (2 ml) and then extracted with Et_2O. The Et_2O layer was dried (anhydr. Na_2SO_4) and concentrated to afford a hydroxy fatty acid fraction. The hydroxy fatty acid fraction was treated with CH_2N_2 to yield corresponding methyl ester **1a** (4.0 mg, 11*S*-hydroxytetradecanoate) and **2a** (4.5 mg, 3*S*,11*S*-dihydroxytetradecanoate), respectively.

Compound **1a**: m.p. 26–28°C; $[\alpha]_D^{20}$ + 1.3 (*c* 0.3, $CHCl_3$); ^{13}C NMR (in $CDCl_3$, 100 MHz) δ: 14.1 (C-14), 18.8, 25.4, 24.7, 25.6, 29.1, 29.2, 29.4, 29.5, 29.6, 34.1, 37.5, 39.7, 51.6 (OCH_3), 71.7 (C-11), and 174.3 (C-1). Its physical and spectral properties were identical to that of (11*S*)-hydroxytetradecanoate (convolvulinic acid methyl ester) [10].

Compound **2a**: m.p. 67–70°C; $[\alpha]_D^{20}$ + 11.5 (*c* 0.5, $CHCl_3$); ^{13}C NMR (in $CDCl_3$, 100 MHz) δ: 14.1 (C-14), 18.8, 25.4, 25.6, 29.4, 29.5, 29.6, 36.5, 37.5, 39.7, 41.1, 51.8 (OCH_3), 68.0 (C-3), 71.7 (C-11), and 173.4 (C-1). Its physical and spectral properties were identical to that of (3*S*,11*S*)-dihydroxytetradecanoate (ipurolic acid methyl ester) [11].

The aqueous layer was neutralized with 5% NaOH and desalted by passage through a Sephadex LH-20 column using MeOH to afford a mixture of sugars (6 mg), from which D-glucose (R_f 0.3), D-quinovose (R_f 0.51), and L-rhamnose (R_f 0.52) were detected by TLC ($CHCl_3$:MeOH:H_2O, 6:4:1) [11]. An aliquot of the mixture was separated by HPLC, using the Thermo Hypersil GOLD Amino column 250 mm × 4.6 mm column, condition: 78% CH_3CN: H_2O, flow rate 0.5 ml/min] to give L-rhamnose [t_R 14.0 min, $[\alpha]_D^{20}$ + 6.8 (*c* 0.5, water)], D-quinovose [t_R 14.2 min, $[\alpha]_D^{20}$ + 40.0 (*c* 0.3, water)], and D-glucose

[t_R 20.1 min, $[\alpha]_D^{20}$ + 90.7 (*c* 0.4, water)]. Another aliquot of the mixture (1.0 mg) was derivatized with Sigma Sil-A for 35 min at 70°C and analyzed by GC–MS [HP-5MS column (30 m × 0.25 mm, 0.25 μm); injection temperature: 250.0°C; column flow: 1.33 ml/min; ion source temperature: 200.0°C; interface temperature: 220.0°C], showing t_R of 9.11, 10.56, and 12.17 min, identical to those of authentic L-rha, D-qui, and D-glc (J&K Chemical®, J&K Scientific Ltd, Beijing, China) derivatives prepared in a similar way, respectively.

3.5 *Alkaline hydrolysis of 3*

Compound **3** (20 mg) was treated with 5% KOH (3 ml) at 85°C for 4 h. The reaction mixture was acidified to pH 4.0 and extracted with Et_2O (3 × 10 ml). The Et_2O layer was dried (anhydr. $MgSO_4$) and concentrated to a small volume (about 0.2 ml) to afford a short chain organic acid fraction. The aqueous layer was further extracted with *n*-BuOH (3 × 20 ml). The *n*-BuOH solution was concentrated *in vacuo* to yield a residue which was subjected to Sephadex LH-20 CC using MeOH to afford a glycosidic acid **2** (15 mg). The short chain organic acid fraction obtained from **3** (1.0 mg) was examined by GC–MS using a Shimadzu GCMS-QP2000 Plus apparatus, equipped with Rxi®-5 ms fused silica capillary column (30 m × 0.25 mm, 0.25 μm). The carrier gas was helium. Column temperature was initially 50°C and increased to 160°C at 20°C/min and to 220°C at 5°C/min, to give one predominant peak which was identified to be angelic acid (t_R 3.7 min): EI-MS: *m/z* 100 $[M]^+$(100), 85 (29), 72 (0.8), 55 (86), 53 (16), and 39 (25).

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